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Tracing organic matter composition and distribution and its role on arsenic release in shallow Cambodian groundwaters

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Abstract

Biogeochemical processes that utilize dissolved organic carbon are widely thought to be responsible for the liberation of arsenic from sediments to shallow groundwater in south and southeast Asia. The accumulation of this known carcinogen to hazardously high concentrations has occurred in the primary source of drinking water in large parts of densely populated countries in this region. Both surface and sedimentary sources of organic matter have been suggested to contribute dissolved organic carbon in these aquifers. However, identification of the source of organic carbon responsible for driving arsenic release remains enigmatic and even controversial. Here, we provide the most extensive interrogation to date of the isotopic signature of ground and surface waters at a known arsenic hotspot in Cambodia. We present tritium and radiocarbon data that demonstrates that recharge through ponds and/or clay windows can transport young, surface derived organic matter into groundwater to depths of 44 m under natural flow conditions. Young organic matter dominates the dissolved organic carbon pool in groundwater that is in close proximity to these surface water sources and we suggest this is likely a regional relationship. In locations distal to surface water contact, dissolved organic carbon represents a mixture of both young surface and older sedimentary derived organic matter. Ground–surface water interaction therefore strongly influences the average dissolved organic carbon age and how this is distributed spatially across the field site. Arsenic mobilization rates appear to be controlled by the age of dissolved organic matter present in these groundwaters. Arsenic concentrations in shallow groundwaters (<20 m) increase by 1 μg/l for every year increase in dissolved organic carbon age compared to only 0.25 μg/l for every year increase in dissolved organic carbon age in deeper (>20 m) groundwaters. We suggest that, while the rate of arsenic release is greatest in shallow aquifer sediments, arsenic release also occurs in deeper aquifer sediments and as such remains an important process in controlling the spatial distribution of arsenic in the groundwaters of SE Asia. Our findings suggest that any anthropogenic activities that alter the source of groundwater recharge or the timescales over which recharge takes place may also drive changes in the natural composition of dissolved organic carbon in these groundwaters. Such changes have the potential to influence both the spatial and temporal evolution of the current groundwater arsenic hazard in this region.

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1. INTRODUCTION

The extensive contamination of groundwaters by geogenic arsenic (As) utilized by millions of people as a primary source of drinking water in South and South East Asia has long been recognised as a public health catastrophe (Chakraborty and Saha, 1987; Balga and Kaiser, 1996; Dhar et al., 1997; Smith et al., 2000; Nickson et al., 1998a; Winkel et al., 2008; Ravenscroft et al., 2009). The consumption of groundwater containing As above 10 μg/l has already resulted in deleterious health effects in millions of people (Yu et al., 2003), with as many as 20% of deaths in arsenic impacted areas of Bangladesh attributable to arsenic (Argos et al., 2010). However, despite more than a decade of active research, several fundamental gaps remain in our understanding of the As release process that limit our ability to better predict locations and anthropogenic activities that risk As contamination. Such information is crucial for governments and those responsible for mitigating the effects of the current crisis and for predicting the potential for secular changes in the As hazard in the future.

The primary source of As in the groundwaters of this region is the rapid weathering of As-bearing rocks in upper Himalayan catchments. This As is then transported by the large rivers that drain these catchments, and deposited in the low-lying young alluvial floodplains of the region. Arsenic is initially sorbed to secondary iron (oxy)hydroxide mineral phases that coat sedimentary grains under aerobic conditions, but is released to solution following the reductive dissolution of these As-bearing phases (Bhattacharya et al., 1997; Nickson et al., 1998b; McArthur et al., 2001; Dowling et al., 2002; Stuben et al., 2003; Horneman et al., 2004; Zheng et al., 2004; Charlet and Polya, 2006). Iron-reducing bacteria catalyse this release of As to solution, with organic matter (OM) critically implicated as an electron donor in this process (Islam et al., 2004; van Geen et al., 2004). However, whilst the biogeochemical processes that are responsible for liberating As to groundwater are now widely understood, identification of the source of OM that drives these processes remains unresolved, elusive and even controversial (Fendorf et al., 2010; Lawson et al., 2013; Neumann et al., 2014).

Several studies have suggested that a sedimentary origin of OM is responsible for driving microbially mediated As release processes; with buried peat (McArthur et al., 2001), aerated root zones and animal burrows (Meharg et al., 2006), or thermally mature hydrocarbons that have migrated from depth (Rowland et al., 2006, 2007, 2008; van Dongen et al., 2008; Al Lawati et al., 2012) amongst suggested potential sources. In contrast, surface derived OM may be utilized in the biogeochemical processes that liberate As, with recharge from ponds, wetlands and through geomorphic features such as abandoned floodplains, meander channel deposits, and scroll bars introducing young dissolved organic carbon (DOC) to shallow groundwaters (Kocar et al., 2008; Papacostas et al., 2008; Polizzotto et al., 2008; Neumann et al., 2010; Lawson et al., 2013). The introduction of this surface derived OM has also been suggested to be exacerbated by the extensive pumping of groundwaters in this region, resulting in the draw down of increased volumes of organic rich recharge waters (Harvey et al., 2002). This particular model is intensely debated (Aggarwal et al., 2003; Harvey et al., 2003; van Geen et al., 2003; Lawson et al., 2008, 2013; Sengupta et al., 2008; McArthur et al., 2011; Neumann et al., 2010; Mailloux et al., 2013), not least because of the implications it holds for future agricultural production in these densely populated countries reliant on rice as a staple food source.

Given the considerable debate surrounding the origin of OM that is responsible for driving As release, the identification and quantification of the different sources of OM present within these aquifer systems is of great importance. This is of particular significance when one considers that it is not necessarily the amount, but the type and reactivity of OM that are the key controls on As release to groundwater (Gault et al., 2005; Rowland et al., 2007; van Dongen et al., 2008; Mladenov et al., 2010). Indeed, it has been suggested that utilisation of different sources of OM will give rise to different rates of As release to groundwaters (Fendorf et al., 2010). Older sources of OM, such as particulate organic carbon (POC) present in buried peat deposits, are likely to have experienced a long history of involvement and consumption in metabolic processes that began immediately following deposition. It is assumed that such metabolic processing may give rise to a less reactive residual OM that may support a slow rate of As release into the groundwater. In contrast, young surface-derived OM that is introduced into the subsurface has had less time to be utilized in metabolic processes, and as such may provide a higher reactivity source of OM that may support a more rapid rate of As release. Distinguishing between the sources of OM present in any groundwater system, and assessing the vulnerability of the system to changes with respect to its dominant OM source, is therefore of critical importance in predicting future spatial and temporal changes in the current As hazard.

In this study we interrogate the isotopic signature of ground and surface waters at a known As hotspot in Cambodia to (i) determine the residence times of groundwater prior to the onset of extensive groundwater pumping, and (ii) characterize and quantify contributions from different sources of dissolved organic carbon present in this aquifer. The chemical composition of the groundwaters at this site has been well characterized in previous studies (Polizzotto et al., 2008; Lawson et al., 2013) and as such will not be discussed in detail here. This study focuses on the radiogenic and stable isotopes of hydrogen (tritium) and carbon ($\delta^{13}C$, ^{14}C) to determine groundwater residence times and provenance OM present in the aqueous phase. In addition, the stable isotopes of oxygen ($\delta^{18}O$) and hydrogen (δD) provide insights into the mode and extent of interaction between ground and surface waters at different locations within the field area. This characterization of predevelopment conditions allow for a robust evaluation of the relative contributions of in-aquifer and surface derived OM where minimal groundwater-pumping-driven drawdown of surface waters prevail. We consider bulk DOC age as a proxy for the residual reactivity of organic matter because it provides an opportunity to account for the time-integrated impact of the reaction history and consumption

it may have experienced. We suggest it is this history that likely controls the remaining potential of residual organic matter for utilization in metabolic processes that could drive As release. This in turn provides an insight into the likely controls on the rate and extent of As release under natural conditions. From this baseline control it will be possible to assess the vulnerability of these aquifer systems to anthropogenic disturbance. In particular, it will provide an opportunity to determine the impact of the extensive pumping of groundwater that is so prevalent in the Bengal basin on groundwater DOC composition and its distribution and ultimately how this influences As release rates to groundwater.

2. MATERIALS AND METHODS

The field area investigated in this study is situated in the Kandal province of Cambodia and covers an area of approximately 50 km^2 between the Mekong and Bassac rivers (Fig. 1). The site has been both geologically, hydrogeochemically and hydrogeologically well characterised by numerous previous studies (e.g. Polya et al., 2003; Benner et al., 2008; Kocar et al., 2008; Polizzotto et al., 2008; Lawson et al., 2013; Sovann and Polya, 2014). Groundwater As concentrations have been reported to exceed 1000 μg/l (Polya et al., 2005; Kocar et al., 2008; Polizzotto et al., 2008; Lawson et al., 2013), with As release shown to occur from near surface river-derived sediments underlying permanently saturated wetlands and abandoned river channels (Berg et al., 2007; Buschmann et al., 2007; Benner et al., 2008; Kocar et al., 2008, 2014; Papacostas et al., 2008; Polizzotto et al., 2008; Rowland et al., 2008; Stuckey et al., 2015a). The site exhibits a relatively simple hydrology; groundwater is recharged in the internal wetland basin and is transported on centennial timescales to the Mekong River (Benner et al., 2008; Kocar et al., 2008). In the monsoon season groundwater flows from the rivers towards the wetlands, with groundwater flowing in the opposite direction for the remaining 8 months of the year (Benner et al., 2008). The simple hydrology at this site reflects natural conditions that would prevail in other As contaminated deltas in the absence of extensive groundwater pumping that otherwise results in the development of complex transient flow paths that make provenancing groundwater difficult (Polya et al., 2005; Polya and Charlet, 2009).

The site geology is characteristic of the floodplains of the lower Mekong basin, with elevated levees along the banks

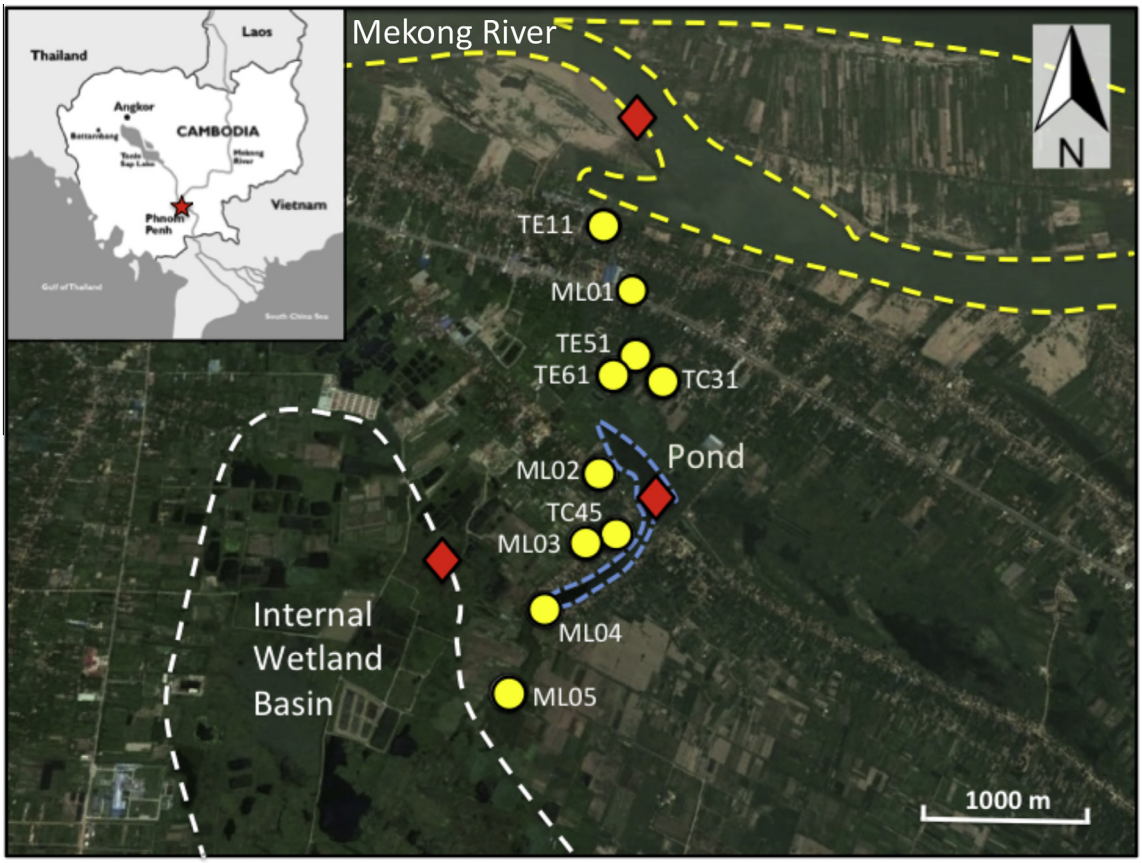

Fig. 1. Aerial image of the field area located approximately 20 km SE of Phnom Penh, Cambodia. The tubewells sampled in this study (yellow circles) lie between the Mekong River (dashed yellow line) in the north and the internal wetland basin (white dashed line) in the south. Also shown are sampled surface waters (red diamonds) and the large pond in the center of the study (blue dashed line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the Mekong and Bassac rivers retreating to a seasonally saturated internal wetland basin that lies between the two rivers (Kocar et al., 2008). The aquifer sands that were targeted for sampling extend to depths in excess of 60 m, and comprise of young Holocene levee/overbank deposits of orange/grey clay containing laminations of peat and silt which overlay fine grey aquifer sands (Tamura et al., 2007; Kocar et al., 2008). Solid phase As concentrations in these sediments vary considerably, with concentrations of 12 mg/kg associated with the surficial clay deposits decreasing to 2 mg/kg in the deeper aquifer sands (Kocar et al., 2008). Clay deposits range in thickness from 3 to 20 m but more commonly are between 10 and 14 m thick (Kocar et al., 2008). The peat here is approximately 5 m thick and typically extends from a depth of approximately 6 m to 11 m (Tamura et al., 2009). This peat has been shown to host a concentrated zone of As enrichment relative to overlying sediments, with arsenic present in the form of arsenian pyrite (Stuckey et al., 2015b). The timing of this peat formation has been shown to be fairly consistent and comparable to that in the Bengal delta at 8.4–6.3 ka (McArthur et al., 2004; Tamura et al., 2009). Older Pleistocene deposits, identified by the orange color of the sands and silts, occasionally underlie the Holocene sediments, and have been reported at depths as shallow as 20 m at this site (Tamura et al., 2009).

A set of twenty groundwater samples were collected from ten well nests (locations where multiple tubewells are present that produce from different depths) in March–April 2009 using standard protocols as described in Lawson et al. (2013). Samples cover a 2.6 km transect perpendicular to the Mekong River with a depth range of 7.3–60 m (Fig. 1). These nests and wells were selected to provide a comprehensive depth coverage and a lateral spatial resolution of no less than one groundwater sample per 0.5 km along the flow path from the wetlands to the Mekong River. Wells are screened over a 3ft interval and drilled as described in Lawson et al. (2013). Given the small producing interval, groundwater is sampled over a small and discrete depth interval and as such minimizes mixing of groundwater over multiple flow paths. Work by Richards et al. (2015) suggests residual contamination from drilling fluids is likely to be less than 3%. A subset of tubewells lying along this transect were also sampled on a monthly basis for stable isotope ($\delta^{18}O$ and δD) analysis to capture the seasonal variability in the hydrological cycle. This work is presented in Lawson et al. (2013) and demonstrated that while surface waters experience significant temporal variability in their isotopic composition, groundwater displays very limited seasonal variability at this study site. However, the chemical composition (including As concentrations) of groundwater has previously been shown to exhibit a high degree of temporal variability at this site (see supplementary information of Polizzotto et al., 2008). As yet there has been no systematic study of the controls on this observed temporal variability. While we recognize that the geochemical composition of groundwater may vary seasonally and that this is likely associated with variable recharge conditions driven by the monsoon and dry seasons, understanding the controls on this variability is beyond the scope of this manuscript and we do not consider this further in this study. A further four surface water samples were collected from the Mekong River and two surface waters locations (the central pond and the internal wetlands delineated in white on Fig. 1) over the course of this transect.

A detailed description of the protocols for geochemical and isotopic analysis is provided in Lawson et al. (2013). Briefly, As and other trace elements were measured with inductively coupled plasma–mass spectrometry and major element concentrations were determined by inductively coupled plasma–atomic emission spectroscopy. Anion analysis of water samples for Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-} was conducted using a Metrohm 761 compact Ion Chromatograph with a Dionex AS9 high capacity column and AG9 high capacity guard column. Stable isotope analysis was performed at the Isotope Community Support Facility, East Kilbride, Scotland using standard techniques. Data are reported as permil variations from the V-SMOW standard and calibrated against both SUERC internal standards (DSW(2), DW2(2) and EKS(2)) and international standards (GISP, V-SMOW and SLAP). $\delta^{13}C$ analysis was performed on a Prism3 (Fisons Instruments) mass spectrometer and calibrated with marble standards (MAB2, medium marble 85/160, $\delta^{13}C = 2.48‰$), internal sodium bicarbonate ($\delta^{13}C$ −4.67‰) and calcium carbonate ($\delta^{13}C$ −24.23‰). Determination of the tritium content of groundwater samples was achieved using the ^{3}He-ingrowth technique developed by Clarke et al. (1976), with measurements of ^{3}He and ^{4}He made at the University of Manchester on a MAP 215 Noble Gas Mass Spectrometer (Mass Analyser Products). Groundwater samples of acidified and sparged $DO^{14}C$, combusted to CO_2, and $DI^{14}C$ acid-hydrolysed to CO_2 were prepared to graphite (Slota et al., 1987). ^{14}C analysis was carried out at the SUERC AMS Laboratory, East Kilbride using either a 5MV tandem accelerator mass spectrometer (Xu et al., 2004) or 250 kV single stage accelerator mass spectrometer (Freeman et al., 2010), both machines by National Electrostatics Corporation, NEC, Wisconsin, US. The ^{14}C enrichment of a sample is measured as a percentage (or fraction) of the ^{14}C activity relative to a modern standard (oxalic acid provided by the US National Bureau of Standards), where 100% modern is defined as the value in AD 1950, in the absence of any anthropogenic influences. Overall analytical precision is quoted at 1σ.

3. RESULTS

3.1. Ground and surface water chemistry

Groundwaters are Ca–Mg–HCO_3 dominated (Tables 1 and 2) typical of most As-bearing groundwaters in this region (Berg et al., 2001; Rowland et al., 2008). Concentrations of dissolved As vary significantly over both lateral and vertical profiles at the study site, with a range from 2 to 1100 μg/l and a mean of 209 μg/l. Spatial and lateral variability in As and dissolved redox sensitive cations and anions is discussed in detail in previous studies at this site (Kocar et al., 2008; Polizzotto et al., 2008; Lawson et al.,

Table 1
Physical and anion composition of groundwaters and surface waters collected from the study site in April 2009.

Sample	Depth (m)	pH	Eh (mV)	Temp (°C)	Cl^- mg/l	NO_3- mg/l	NH_4^+ mg/l	ΣPO_4^{3-} mg/l	ΣSO_4^{2-} mg/l	Br^- mg/l	HCO_3^- mg/l
TE11-12	12	6.4	222	30.0	71	72	ND	ND	37	ND	500
TE11-20	20	6.8	−29	29.6	114	8.8	ND	ND	63	0.2	609
TE11-55	55	6.4	−73	29.8	3.1	1.1	30	0.4	0.2	0.1	511
ML01-9	9	6.1	−44	28.8	64	0.1	12	0.9	7.4	0.2	563
ML01-29	28.6	6.8	−44	30.2	7	ND	15	0.5	0.4	ND	410
ML01-37	37	7.0	−27	30.1	13	ND	15	0.4	0.5	ND	363
TE51-12	12	6.6	−30	34.0	14	0.5	57	0.2	0.6	0.2	465
TE51-20	20	6.9	−116	30.7	5.5	0.1	22	1.2	<0.05	0.3	404
TC31	51	6.8	−76	30.1	5.2	7	50	0.5	0.1	1.1	659
TE61	48	6.3	−100	30.2	4.8	ND	80	ND	ND	0.7	757
ML02	8.5	6.5	−163	29.9	61	ND	0.1	0.5	12	ND	444
TC45-12	12	6.3	−117	31.1	325	0.4	40	3.4	26	0.5	817
TC45-20	20	6.4	135	31.1	479	56	0.5	ND	146	0.7	631
ML03-7	7.3	6.4	−47	29.1	45	0.4	ND	0.3	26	ND	292
ML03-24	23.8	6.1	−70	29.2	30	57	0.3	2.4	0.7	ND	123
ML03-42	42	6.7	ND	30.0	1520	0.3	7.0	1.7	3.3	<0.05	304
ML04-8	8.2	6.4	14	30.4	56	11	ND	<0.05	25	0.2	689
ML04-30	29.1	7.1	60	31.4	21	2.4	ND	ND	2.8	<0.05	187
ML04-44	44	6.9	179	31.2	22	7	ND	ND	4.6	ND	169
ML05	60	6.5	−36	33.2	3.7	20	ND	0.9	0.2	ND	244
Wetlands			ND	ND	26	0.1	1.8	0.4	3	ND	170
Pond			ND	ND	20	0.5	ND	ND	0.8	0.05	176
River Mekong			ND	ND	5.4	1.1	ND	0.2	5.1	ND	62

ND = not determined.

Table 2
Major and minor cation analysis of groundwater samples collected from study site during April 2009.

Sample	DOC mg/l	As ug/l	Fe mg/l	Mn µg/l	Ca mg/l	K mg/l	Mg mg/l	Na mg/l
TE11-12	0.8	6	0.0	109	127.4	1.7	41.6	45.8
TE11-20	1.1	346	14.6	295	135.2	2.2	43.9	100.1
TE11-55	5.1	829	6.7	82	61.2	2.8	16.8	67.7
ML01-9	1.9	212	17.3	915	95.1	2.4	29.7	49.3
ML01-29	6.8	217	2.2	799	45.4	4.6	9.5	27.6
ML01-37	6.5	258	6.2	12,760	40.6	3.6	8.4	19.4
TE51-12	3.8	418	13.1	677	95.5	3.2	26.0	21.4
TE51-20	10.9	1100	2.2	10,187	44.2	7.2	10.7	35.6
TC31	15.3	46	0.0	469	86.1	9.3	20.4	55.9
TE61	11.6	44	0.2	106	76.6	7.3	28.4	29.9
ML02	6.8	4	1.2	474	38.0	1.5	10.7	75.5
TC45-12	4.9	3	3.0	262	194.6	2.0	68.5	138.2
TC45-20	2.5	2	0.4	189	240.8	0.6	92.1	165.4
ML03-7	3.7	10	0.9	11,581	34.7	1.2	15.0	56.6
ML03-24	6.5	35	15.3	477	35.7	2.4	10.1	35.8
ML03-42	63.4	32	0.0	511	52.4	3.0	14.1	58.3
ML04-8	2.2	9	7.8	533	135.4	0.7	42.3	198.3
ML04-30	6.2	13	0.2	88	37.5	5.1	10.2	21.3
ML04-44	6.4	30	15.0	367	42.6	5.0	12.0	21.0
ML05	3.1	778	3.5	323	42.3	1.7	14.9	30.0
Wetlands	6.7	10.2	0.2	207	32.38	5.84	10.14	21.01
Pond	6.1	3.3	0.2	150	31.92	4.38	10.20	19.47
Mekong	2.4	1.2	0.1	0.8	7.3	1.5	2.4	5.7

2013) and as such is not described in detail here. Nonetheless, we highlight here a region of high As concentrations over the whole depth profile within 1 km of the Mekong River and near the internal wetlands, 2.6 km from the Mekong River. Arsenic concentrations are lower (maximum 35 µg/l) in the centre of the study area and associated

with the presence of a large pond (Kocar et al., 2008; Polizzotto et al., 2008; Lawson et al., 2013).

3.2. Stable isotopic composition of ground and surface waters

The connectivity and degree of interaction between groundwater and surface waters was investigated by comparing the isotopic signature (δD and $\delta^{18}O$) of groundwaters from the study site with that of Mekong River, wetland and pond waters located at different points along the transect. A cumulative monthly sample of precipitation was also analysed for the development of a working local meteoric water line (LMWL) from which deviations in the isotopic signature of ground and surface water can be determined. Fig. 2 shows the variation in the isotopic composition of local rainwater, groundwater, Mekong river and surface waters. The LMWL has a gradient of 8.3, which is similar to that of the global meteoric water line (GMWL) of 8.17 (Rozanski et al., 1993) and within the range of gradients (7.95–9.11) determined by Kabeya et al. (2007) for the nearby Kampong Thom province – as such we consider it a reasonable working LMWL for this site. The D excess of the local precipitation of between 8.1 and 17.6 (given here relative to a gradient of 8) is indicative of a contribution of re-evaporated local surface waters to the precipitation, which is typical for such a humid climate (Clark and Fritz, 2000).

Groundwater samples typically fall on or below the LMWL, with a trend to more isotopically enriched values characteristic of surface waters signatures and indicative of contributions from an evaporated source of recharge to the groundwater. The similarity in the gradients of the regression lines between groundwaters (gradient = 5.35) and the wetland and ponds (gradient = 6.1) suggests that surface waters are the most likely source of isotopically enriched recharge to groundwater. These regression lines are calculated by considering the highly variable monthly isotopic composition as measured in Lawson et al. (2013). These gradients are also characteristic of evaporative trends for theoretical evaporation at 70–85% humidity, in line with the range of average monthly humidities for this location.

3.3. Tritium concentrations and residence times of ground and surface waters

The tritium content in precipitation from the nearest IAEA GNIP station at Bangkok from 1953 to 2009 is presented in Fig. 3 below. Here it can be seen that the present day tritium content is approximately 2–4 tritium units (TU), and has remained below 6 TU since 1984. We discuss here tritium concentrations previously measured in the study of Lawson et al. (2013). The tritium content of the Mekong River of 3.5 ± 0.2 TU presented in Table 3 is thus consistent with current levels in precipitation and provides a constraint on the initial tritium content of recharging waters.

Tritium concentrations in the groundwater of less than 3 TU suggest that infiltration took place after the cessation of atmospheric bomb testing, which would otherwise exceed 10 TU in low latitude regions when residual "bomb" tritium is present (Clark and Fritz, 2000). This is because the natural decay of tritium in groundwater is significantly slower than the decrease in tritium concentrations in precipitation due to the preferential retention of the isotopically heavier tritium-bearing isotopologue of H_2O in the oceans. If we assume no hydrodynamic dispersion or mixing, which

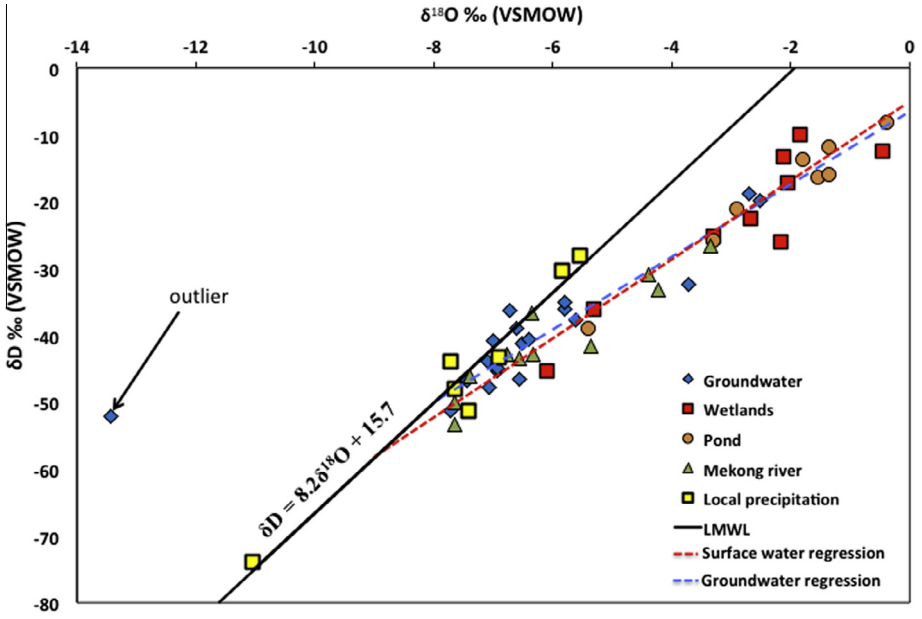

Fig. 2. δD vs $\delta^{18}O$ plot of groundwaters, surface waters and precipitation at the study site in the Kien Svay region, Kandal Province, Cambodia. Groundwater samples were collected in April 2009, with surface waters and precipitation ($n = 7$) collected approximately monthly over the year. Regression lines are given for surface waters (slope of 6.1) and groundwaters (slope of 5.4). The groundwater with measured $\delta^{18}O < -13‰$ is an outlier (Dixon's Q test; 99% confidence interval) and excluded from the derivation of the groundwater regression line.

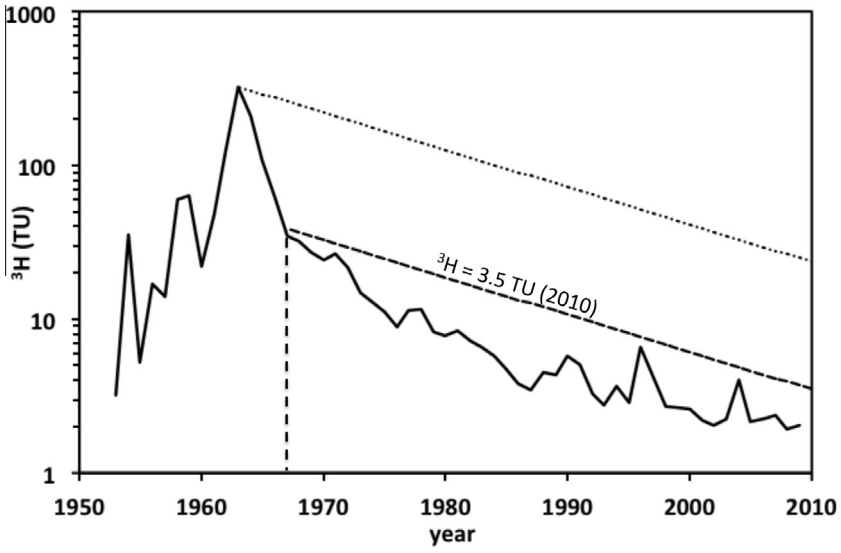

Fig. 3. ^{3}H concentration in precipitation. Data for the period 1969–2009 taken from the IAEA GNIP database for the nearest monitoring station at Bangkok (IAEA/WMO, 2006). Data for the period 1953–1968 was calculated from ^{3}H concentration data presented in Stute (2001), using a correction factor of 1.84. The dashed line represents a compositional trajectory for samples containing 3.5 TU in 2010, and intercepts the tritium in precipitation profile in 1967. Also shown for reference is the decay of bomb peak tritium. Should this be present this would manifest as 2010 tritium concentrations of 23.6 TU, exceeding measured concentrations by an order of magnitude.

Table 3
Summary of ^{3}H concentrations for groundwaters and surface waters and uncorrected and modeled radiocarbon of DIC based mean groundwater residence times. Errors are given as 1σ of the tritium concentration. Tritium ages are given for two tritium input functions. * assumes a 3.5 TU (present day) and # assumes a 38 TU (maximum historic tritium concentration in precipitation observed in 1967) input function. Modeled values could not be determined for locations TE61 and ML03-40 because key input parameters were shown to lie more than 2σ from mean values, and as such considered to be outliers.

Sample	δ^{13}C (‰)	^{14}C (pmC)	$\pm\sigma$	^{3}H (TU)	$\pm\sigma$	^{3}H age* (years)	^{3}H age# (years)	Uncorrected DIC Age	Modeled Age
TE11-12	−13.1	100.54	0.46	2.53	0.14	5.8	>43	>0	>0
TE11-20	−15.2	102.62	0.41	2.01	0.11	9.9	>43	>0	>0
TE11-55	−15.8	60.71	0.28	0.00		>60	>43	4126	3053
ML01-10	−16.0	101.49	0.41	1.35	0.08	17	>43	>0	>0
ML01-30	−14.1	74.06	0.31	0.00		>60	>43	2483	457
ML01-40	−12.3	72.23	0.34	0.00		>60	>43	2689	>0
TE51-12	−8.7	99.71	0.42	2.22	0.12	8.2	>43	24	>0
TE51-20	−11.3	78.26	0.39	0.00		>60	>43	2026	>0
TC31-51	−17.6	85.7	0.41	0.00		>60	>43	1275	1078
TE61-48	1.1	89.03	0.39	0.00		>60	>43	961	DNC
ML02-8	−17.8	61.03	0.33	1.55	0.08	14.6	>43	4082	3966
TC45-12	−14.9	84.95	0.31	1.91	0.11	10.9	>43	1348	>0
TC45-20	−15.0	96.78	0.41	1.89	0.10	11	>43	271	>0
ML03-10	−14.5	100.77	0.42	1.78	0.09	12.1	>43	>0	>0
ML03-20	−7.7	66.93	0.38	1.63	0.09	13.7	>43	3319	>0
ML03-40	−3.4	41.51	0.37	2.01	0.10	10	>43	7268	DNC
ML04-8	−16.3	81.59	0.38	2.06	0.11	9.5	>43	1682	839
ML04-30	−19.6	93.16	0.49	2.65	0.14	5	>43	586	1259
ML04-44	−13.3	94.73	0.46	2.24	0.12	8	>43	448	>0
ML05-60	−14.4	74.63	0.28	0.00		>60	>43	2419	581
Wetlands				1.91	0.11				
Pond				2.03	0.11				
Mekong River				3.50	0.18				

is reasonable given that groundwater flow at this site has been minimally disturbed by groundwater pumping, then estimates of groundwater mean residence times (MRT) can be made from measured tritium concentrations and assumed tritium input functions through the following equation:

$$t = -17.93 \ln \frac{a_t {}^3H}{a_o {}^3H} \quad (1)$$

where t is the mean residence time, a_t^3H is the residual tritium activity of the sample, a_o^3H is the tritium input function, and -17.93 is the unitless constant to account for the decay of tritium to ^3He (Clark and Fritz, 2000). We discuss our data in the context of mean residence times, and not groundwater ages, because groundwaters very rarely comprise water of a single age. Instead, they more frequently comprise mixtures of waters along flow paths of different ages. Table 3 presents tritium concentrations for each of the wells and surface waters sampled, and provides MRTs based on two tritium input functions that allow us to bracket the possible MRTs at each location. A tritium input function of 3.5 TU was chosen to represent the tritium concentration of present day precipitation at the study site based on concentrations of tritium in the Mekong River. A second tritium input function of 38.5 TU was selected to represent the largest possible input function for groundwaters that recharged after the cessation of thermonuclear bomb testing and is based upon the tritium concentration in precipitation which fell in 1967 (Fig. 3). This was determined by back tracking along a decay line from the present day concentration of 3.5 TU in Mekong River water to the two points at which the decay line intercepts the tritium concentration in precipitation profile. The upper profile Fig. 3 represents the temporal evolution in groundwater tritium concentrations should the bomb peak be present in our samples. The predicted tritium concentration of 23.4 TU in 2010 is over an order of magnitude greater than almost all measured concentrations, which we consider as evidence for the absence of bomb tritium in our samples. Given the absence of peak bomb tritium in our samples after accounting for natural decay, we do not consider the second point at which the decay curve intercepts the tritium concentration in precipitation profile in 1958 as a likely maximum age for tritium-active samples. As such, the maximum possible MRT of any tritium-active sample in this study site cannot exceed 43 years (assuming recharge in 1967 and sample analysis in 2010). However, given that independent sampling of ^3He and noble gases was not possible for this study site, we are not able to determine more precise ages of these groundwaters.

Groundwater was shown to contain an active contribution of modern (<43 years) recharge in 13 of the 20 wells sampled at this study site, and reaches depths of up to 44 m at some locations. The tritium concentrations for tritium-active groundwaters range from 2.65 ± 0.14 TU at site ML04 at a depth of 30 m to 1.35 ± 0.08 TU at site ML01 at a depth of 9 m. This gives a range in groundwater MRT of 5 ± 0.27 years to 17 ± 0.94 years when the 3.5 TU tritium input function we define here is applied and represents the minimum likely MRT of these groundwaters. All tritium-active groundwaters give a MRT greater than 43 years when the 38.5 TU tritium input function is applied, placing a consistent upper limit for tritium-active samples. Groundwater at depths less than 12 m displayed contributions of modern recharge over the entire site, with a range in concentrations of 1.35 ± 0.08 TU at site ML01 to 2.53 ± 0.14 TU at site TE11. Of the 6 intermediate depth (20–30 m) groundwaters sampled, 4 were found to be tritium-active with tritium concentrations of 1.63 ± 0.09 TU–2.65 ± 0.14 TU, representing minimum MRTs of 13.7 ± 0.74 years and 5 ± 0.27 years respectively. In contrast, only 2 of the 7 deep (>30 m) groundwater samples were found to be tritium-active, with concentrations of 2.01 ± 0.10 and 2.24 ± 0.12 TU reported for sites ML03 and ML04 at depths of 42 and 44 m respectively. Tritium dead groundwaters (below the minimum detectable limit of 0.2 TU) were found from depths of 20 m at site TE51 to the maximum depth of sampling at 60 m at site ML05.

The variability in MRTs with depth gives rise to a spatial distribution that allows identification of the locations of rapid recharge through high permeability sediments to underlying groundwater at this site. The presence of tritium-active groundwater suggests an active component of surface water recharge along the entire 2.6 km profile. Groundwater was shown to be tritium-active in both the shallow and intermediate depths at site TE11. This is consistent with stable isotope data and previous hydraulic head measurements and monitoring of Mekong River water levels that suggest that Mekong River water is ingressing into the aquifer at this location (Benner et al., 2008; Lawson et al., 2013). Three well nests in the centre of the study area report tritium-active groundwater over the entire depth profile (TC45, ML03 and ML04). These groundwaters are all located more than 1.4 km from the Mekong River and as such are outside of the influence of ingressing Mekong River water. Stable isotope data at these locations suggest a possible influence from recharge from the large pond located in close proximity to these well nests (Lawson et al., 2013).

Arsenic concentrations are typically lower in tritium-active groundwaters compared with tritium-dead groundwaters. The concentration of As exceeded 10 μg/l in 7 of the 13 tritium-active groundwaters Fig. 4), with a range of 2–418 μg/l and a mean As concentration of 86.2 μg/l. In contrast, all of the tritium-dead groundwaters contain concentrations of As that exceed 10 μg/l, ranging from 44 to 1100 μg/l and with a mean As concentration of 467 μg/l. Interestingly, three groundwater samples were found to be tritium-active and have As concentrations that exceed 100 μg/l. Sample TE11-20, which has an As concentration of 346 μg/l, appears to be located within the sphere of influence of ingressing Mekong River water during the rainy season. Groundwater at this location has been shown to flow from the internal wetlands to the Mekong River over centennial timescales. The modern tritium signature in groundwaters at this location may arise as a result of mixing between older, high-As groundwater that has migrated from the wetland basin with tritium-active Mekong River water. Similarly, locations ML01-10 and TE51-12 are located in the zone of high As concentrations within 1 km of the Mekong River but are also tritium-active. This may either reflect hydrologic transport of As from upstream into groundwater that has an active component of modern recharge from above or a rapid removal of oxidants from the system during recharge thus developing the reducing conditions that are required for As mobilisation.

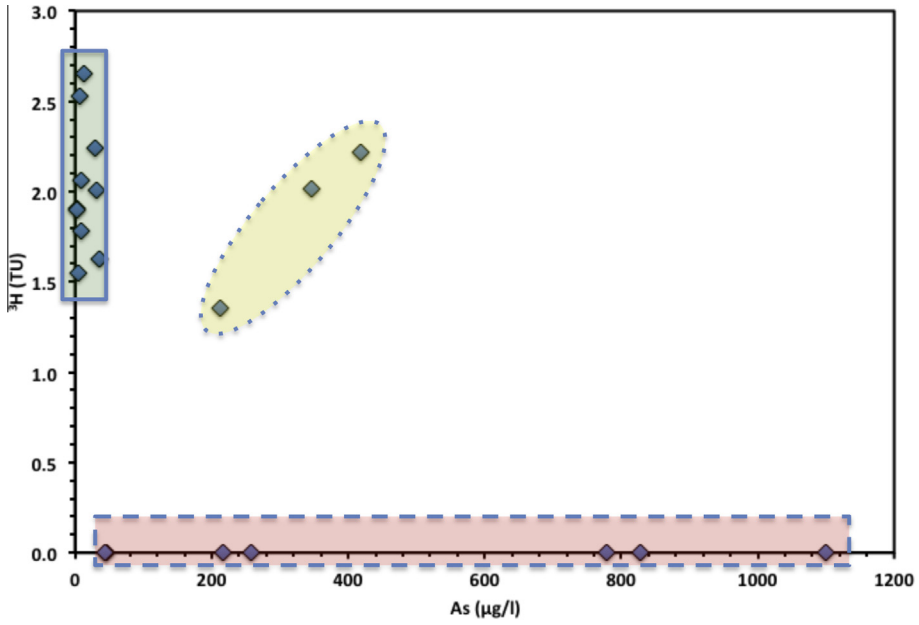

Fig. 4. Distinct groups of groundwaters discriminated by ^{3}H and dissolved As. (i) tritium-active groundwaters with As = 2–35 µg/l (highlighted by green rectangle demarked by solid lines), (ii) tritium-active groundwaters with As > 200 µg/l (highlighted by yellow oval and demarked by dotted lines), and (iii) tritium-dead groundwaters with highly variable (44–1100 µg/l) As (highlighted by red rectangle and demarked by dashed lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.4. Dissolved inorganic carbon radiocarbon concentrations and groundwater residence times

We present here uncorrected radiocarbon ages that are calculated from the measured concentration of ^{14}C of dissolved inorganic carbon (DIC) assuming exponential decay of ^{14}C in DIC as a function of its half-life. A detailed description of radiocarbon dating is outside of the scope of this study, and we refer the reader to Clark and Fritz (2000) for details. It is widely accepted that uncorrected ^{14}C groundwater ages often appear to over predict the true age of the sample. This is because contributions of ^{14}C-dead inorganic carbon associated with processes such as carbonate dissolution result in the dilution of ^{14}C activity in the sample. In this study, we applied the correction model of Clark and Fritz (2000) to correct measured radiocarbon ages and determine MRTs at this study site for groundwaters older than the 60 years covered by the tritium based technique discussed above. This model utilizes isotopic measurements to calculate the dilution from ^{14}C-dead inorganic carbon given that any process that adds, removes or exchanges carbon with the DIC reservoir would likely alter both the ^{14}C activity of the groundwater and the δ^{13}C signature of DIC. This model accounts for isotope evolution in the saturated zone by dissolution and two component mixing between the constant δ^{13}C values of soil CO_2 and inorganic carbon from carbonate dissolution. In addition to this, the model accounts for the variable enrichment of the δ^{13}C signature that arises because of these reactions and equilibration between CO_2(g) and the dissolved carbonate species in the unsaturated zone. In this study, a δ^{13}C of −22.9‰ is assumed to be representative of the initial soil CO_2 reservoir. This represents the mean value of δ^{13}C of dissolved organic carbon determined for these groundwaters.

The uncorrected ^{14}C ages of DIC range from modern (values > 100% modern i.e. containing post AD1950 carbon) at sites TE-11, ML01 and ML03 to 7268 ± 24 years BP for groundwater at ML03 at a depth of 50 m (Table 3). In contrast, modelled groundwater residence times range from modern in 11 of the groundwaters sampled to 3966 ± 27 years BP at site ML02 at a depth of 8 m. The ^{14}C activity does not show any consistent trend along the transect but does decrease with depth in four of the six well nests, suggesting an increase in age and/or contributions of ^{14}C-dead DIC with depth.

3.5. Radiocarbon ages of dissolved organic carbon

The radiocarbon age of DOC varies significantly in the groundwater at this study site, with a range of ^{14}C DOC ages from 4036 ± 38 years at site TE11 at a depth of 55 m to modern at depths of 30 and 44 m at site ML04 (see Table 4). Radiocarbon ages of DOC at this site have previously been shown to be almost exclusively younger than sedimentary organic matter (SOM) for equivalent depths (Tamura et al., 2009; Lawson et al., 2013).

A depth dependent variation in the rate of As release per year increase in the age of groundwater DOC is observed from the comparison of shallow and deep groundwaters that are tritium dead or contain As concentrations above 100 µg/l when tritium is present (Fig. 5). Shallow groundwaters (<20 m) accrue As at a rate of approximately 1 µg/l for every year increase in associated DOC age compared

Table 4
Carbon isotope signatures ($\delta^{13}C$ and ^{14}C) and derived C-14 ages for dissolved organic carbon in groundwater at the study site. Note that samples MLO4-30 and ML04-44 contain modern organic carbon signatures, indicating the dominance of surface derived organic carbon in DOC at these depths. ND for tubewell ML04-8 denotes not determined – insufficient sample material.

Tubewell	Depth (m)	C-14 enrichment (% modern)	+/−	C-14 age (yrs BP)	+/−	$\delta^{13}C$ (‰)
TE11-12	12	99.07	0.46	75	37	−5.3
TE11-20	21	87.94	0.41	1032	37	−18.3
TE11-55	55	60.50	0.28	4036	38	−18.5
ML01-9	9	93.83	0.41	512	35	−13.4
ML01-29	29	71.65	0.31	2679	35	−25.0
ML01-37	37	72.57	0.34	2575	37	−26.5
TE51-12	12	91.08	0.42	751	37	−27.3
TE51-20	20	85.47	0.39	1261	37	−25.7
TC31	51	89.99	0.41	847	36	−26.6
TE61	48	89.61	0.39	881	35	−26.6
ML02	9	75.06	0.33	2304	35	−26.2
TC45-12	12	71.03	0.31	2748	35	−19.1
TC45-20	20	93.75	0.41	519	35	−21.6
ML03-7	7	91.45	0.42	718	37	−21.6
ML03-24	24	87.88	0.38	1038	35	−26.9
ML03-42	42	83.52	0.37	1447	35	−24.4
ML04-8	8	ND	ND	ND	ND	ND
ML04-30	29	105.38	0.49	<50	50	−29.3
ML04-44	44	100.71	0.46	<50	50	−26.2
ML05	60	64.80	0.28	3485	35	−26.2

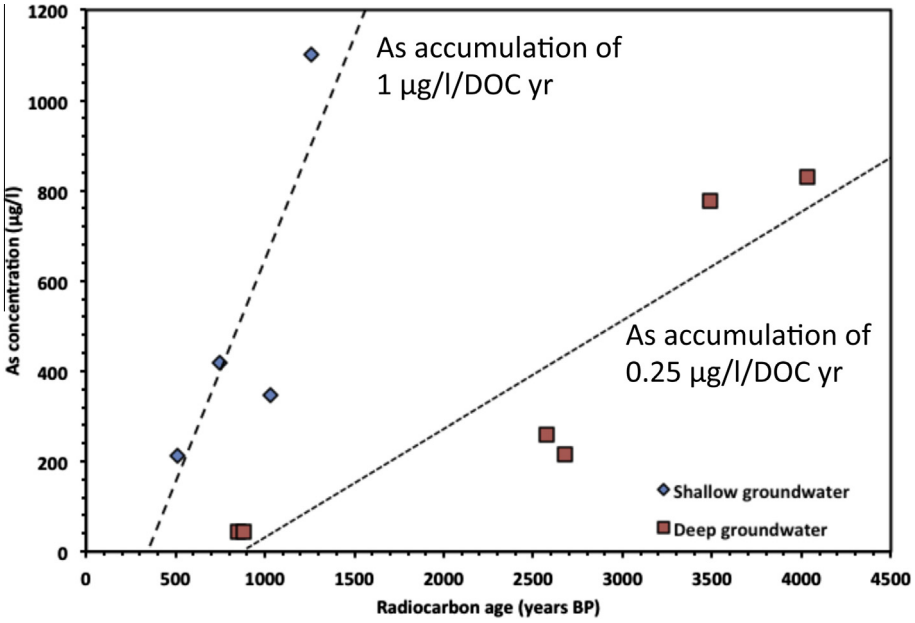

Fig. 5. Contrasting release rate (with respect to DOC radiocarbon age) of arsenic in (i) shallow (9–20 m) and (ii) deep (20–60 m) groundwaters, where As concentrations exceeds 10 µg/l and the radiocarbon age is not modern. As concentrations in shallow groundwaters are shown to accumulate at a rate that is four times greater than that in deep groundwaters (~1 µg/l/DOC yr vs ~0.25 µg/l/DOC yr).

to approximately 0.25 µg/l for every year increase in DOC age in deep groundwater (20–60 m). This data suggests that older DOC in deeper groundwaters is also able to support As release within the aquifer matrix, albeit at a lower rate of accumulation relative to the age of the associated DOC. This observation is consistent with our assumption that the age of DOC may be an appropriate proxy for organic carbon reactivity. These depth categories were chosen to reflect recharge through shallow surficial sediments, potentially dominated by clays that extend to depths of up to 20 m at this site (Kocar et al., 2008), and deeper aquifer sands. We focus here only on high arsenic or tritium dead waters in this assessment because Lawson et al. (2013) have previously shown that the low-As groundwater

underlying the pond in central region of our study area is dominated by contributions of young pond derived recharge over its entire depth profile. While this recharge introduces modern surface derived DOC, it also has been shown to introduce oxic waters, giving rise to groundwater sulfate concentrations in excess of 200 mg/l (Lawson et al., 2013). As a result, we suggest that the relationship between the age of DOC and As concentration in this region of the site is decoupled because of the impact of oxidants that immobilize As through sorption to Fe(III) phases and likely consume the co-transported surface derived DOC. In contrast, where oxic waters are not present anaerobic processes dominate the consumption of DOC. This may ultimately lead to As release from sediments and may support its continued mobility in the genesis of high-As groundwaters.

4. DISCUSSION

The unresolved debate as to what source of OM is responsible for driving As release remains one of the few gaps in the understanding of the As release process that limits the ability to predict how, when and where the current As hazard may change in the groundwaters of South and South East Asia. Site-specific variability in the sedimentary profile and the occurrence of high As groundwaters in locations where groundwater pumping is not common practice have led some to suggest that surface (e.g. Sengupta et al., 2008; McArthur et al., 2011) or sedimentary sources (e.g. Mailloux et al., 2013) of OM cannot be responsible for the generation of high As groundwaters at these sites. However, the lateral transport of OM from subsurface sources and transport of modern surface derived OM could give rise to a pre-development groundwater DOC pool that is made up of contributions from a variety of sources of OM, with both surface and subsurface sources present. If this is the case, the relative contributions of these different sources could control As release rates in these groundwaters (Gault et al., 2005; Rowland et al., 2007; van Dongen et al., 2008; Mladenov et al., 2010; Fendorf et al., 2010). The potential for groundwater pumping practices to change the relative contributions from these different OM reservoirs (e.g. Harvey et al., 2002) must also be considered.

4.1. Hydrological environment

Previous studies at this site have demonstrated significant ground–surface water interaction (Benner et al., 2008; Lawson et al., 2013). Lawson et al. (2013) show that shallow (<12 m) groundwater is tritium-active over the entire site. This observation conflicts with modelled travel times of 200 years for the migration of recharge waters to depths in excess of 10 m at this site (Benner et al., 2008). This suggests that recharge along natural, rapid flow paths takes place from surface waters or through highly permeable clay windows in direct hydraulic continuity with the groundwater, and that these contributions dominate the shallow groundwater recharge budget at this site. Such conduits have recently been proposed to develop through the burrowing action of crabs providing widespread direct recharge conduits through low permeability surficial sediments to underlying aquifer sands (Stahl et al., 2014).

Of particular importance from previous studies are the observations that there are significant contributions of modern recharge from the large pond to groundwater in the center of the study site 1–2.2 km from the Mekong River (Benner et al., 2008; Lawson et al., 2013).

Modelled residence times of DIC are internally consistent with residence times based on tritium measurements (i.e. provide modern ^{14}C based residence times where tritium is present and older residence times where tritium is absent) in thirteen of the eighteen groundwaters where a correction for dilution of ^{14}C was possible. Interestingly, four shallow groundwater samples (TE11-12, TE11-20, ML01-10 and ML03-10) containted ^{14}C values indicative of recharge during the last 50 years. The observation of modern DIC in groundwater at depths of 12 and 20 m at site TE11 further supports the previous inference that these locations are influenced by ingressing Mekong river water (Lawson et al., 2013). In contrast, the modern DIC at ML01 in shallow groundwater provides additional evidence for the requirement of rapid recharge through surficial clays, with ML01 not located within close proximity to any surface water body.

The groundwater residence time at TE11 at a depth of 55 m of 3053 years in tritium dead groundwater likely represents the upper limit for mean residence times at this study site given that the groundwater at ML02, despite having an older apparent modelled radiocarbon based residence time, is tritium active. The MRT of TE11 at a depth of 55 m is, to first order, consistent with modelling estimates of groundwater age at this location that predict centennial timescales for groundwater flow from the wetland basin to the Mekong River (Benner et al., 2008). Similarly, our modelled MRT of 581 years in tritium dead groundwater at a depth of 60 m at ML05 is in line with age estimates in excess of 280 years for recharge through surficial clay deposits near the wetland basin (Benner et al., 2008).

There are three samples (ML02-8, ML04-8 and ML04-20) where radiocarbon based MRTs exceed constraints provided by co-existing tritium in these groundwaters. We suggest that an alternative source(s) of diluting DIC is made to the groundwater at these sites that is not considered in our age-correction model. Bethke and Johnson (2002) show that mixing of old waters that have been trapped in aquitards with younger groundwater in aquifers occurs at a rate that is controlled only by the volume ratio of fluid in aquitards relative to fluid in aquifers, and is independent of the actual rate of the contribution (a function of permeability). Given that these samples are taken from shallow tubewells that clearly contain significant contributions of young recharge, a large contribution of older water must be sourced from the extensive clay deposits within this vicinity.

This mixing of modern recharge through high permeability sediments and fluids that slowly migrate through clay deposits could have significant implications for the release and spatial distribution of As in the groundwater at this location. Clays have been suggested to be a possible source of arsenic to groundwater at this site and elsewhere

regionally (Erban et al., 2013), and as such one may anticipate high As concentrations associated with mixed fluids that contain a component of recharge from these low permeability sediments. However, the groundwater in this region of the transect contains some of the lowest As concentrations measured at this study site over the entire depth profile. These results are more consistent with modelling results from the recent study of Kocar et al. (2014) who suggest that concentrations of As are likely to be low in groundwaters where contributions of high As recharged from low permeability sediment are overwhelmed by recharge through nearby high permeability sediments.

Interestingly, the study of Polizzotto et al. (2008) measured highly variable concentrations of As at site TC45-20, also located within 100 m of this pond, with both relatively high (99 μg/l) and low (9 μg/l) concentrations reported. These are higher than the concentration of As we measured for this location (2 μg/l). Nonetheless, these results broadly support the findings of the recent study by Stuckey et al. (2015a) who suggest that groundwater underlying seasonally saturated water bodies is likely to be characterized by relatively lower concentrations of As because it experiences periods where oxic recharge drives aerobic metabolisms that consume reactive DOC. This process reduces the reactivity of residual DOC for anaerobic processes that may develop deeper in the sediment, rendering it less capable of driving extensive As release.

In contrast to the low As concentrations associated with tritium active groundwater in the center of the field site, we observe high concentrations of As where radiocarbon-based MRT estimates are consistent with the absence of tritium in groundwater (Lawson et al., 2013). The relationship we observe between low As concentrations in tritium-active groundwaters and higher concentrations of As in older groundwaters at similar depths suggests that the mode and timescales of recharge plays a significant role in the genesis of high As groundwaters. Older groundwater at the same depth as young groundwater elsewhere requires large differences in the vertical permeability profile of sediments spatially. Low permeability sediments have previously been shown to act as a barrier to oxidants and lead to the development of reducing conditions (van Geen et al., 2006). This control on As distribution has also been identified in numerous other studies that link high As groundwaters with geomorphologic and surface features such as abandoned or existing channels, swamps and ox bow lakes (Nath et al., 2005; Acharyya and Shah, 2007). These features have been shown to be areas where the rapid deposition of OM occurs, the decomposition of which facilitates the release of As to groundwaters (Papacostas et al., 2008; Quicksall et al., 2008).

4.2. Organic matter sources to groundwater

The radiocarbon age of DOC, while consistently younger than SOM at similar depths (Lawson et al., 2013), is typically older than co-existing groundwater at this study site. This is consistent with DOC concentration depth profiles that increase with depth and requires a subsurface, sedimentary contribution of DOC to the groundwater DOC pool. This requirement for a contribution from a sedimentary organic carbon pool supports the experimental work of Neumann et al. (2014) who suggest that perturbations to the aquifer matrix could promote the mobilization of bioavailable organic carbon from aquifer sediments. C-14 measurements of the sediment from three drill cores at this site place an upper and lower age limit of 8.4–6.3 kyrs on peat that are present from 6 m to 14 m (Tamura et al., 2009), with deeper sediments shown to contain SOM with C-14 ages of up to 9.0 kyrs (Lawson et al., 2013). Based on these constraints, it has been shown that radiocarbon ages of DOC appear consistent with mixing of 1 mg/l of modern (age corrected) OM with sedimentary derived OM with ages of between 1000 and 6000 years (Lawson et al., 2013).

Given that groundwater DOC ages can be explained by mixing of age corrected modern surface OM and sedimentary OM between 1 and 6 kyrs, a maximum estimate of the relative contributions of surface derived OM and sedimentary derived OM can be calculated (Table 5). From this it can be seen that as the age of the sedimentary OM end member increases, the contributions of surface derived modern OM must also increase to produce the observed DOC age. Similarly, where modern DOC is present, the majority of the DOC must derive from modern surface derived OM. Shallow groundwater is shown to frequently contain a large component of young surface derived OM, with the relative contributions of this young OM typically decreasing with increasing depth. These calculations suggest that sedimentary organic matter can comprise anything from 95% of the total DOC pool at site TC45 at a depth of 12 m to very small relative proportions of DOC with a modern signature at site ML04 at depths of 30 and 44 m.

These estimates represent an upper limit on the possible contributions of modern OM to the groundwater DOC pool because they only consider two-component mixing of one modern organic carbon source and one old sedimentary organic carbon source. It is more likely that DOC accumulates from different sources over the course of a flow path during which time a fraction of the DOC will be removed following its involvement in biogeochemical processes. In such a scenario the age of the DOC in the groundwater is actually equivalent to the weighted integrated mean age of the different contributions of DOC along the flow path that remains in the groundwater. As such, the data presented here is heavily model dependent and likely represents an over-simplification of the actual processes associated with the liberation and removal of DOC in groundwater. Nonetheless, this demonstrates that DOC in groundwater must derive from numerous sources and that even in pre-development conditions a significant amount of the total DOC pool derives from a surface source of OM.

The presence of modern bulk DOC in shallow groundwater conflicts with several modeling studies that suggest that modern DOC can only reach depths of a few meters following recharge (Datta et al., 2011; Mailloux et al., 2013; Kocar et al., 2014). This disparity between modeled and measured transport times for DOC at different sites demonstrates the importance of high-permeability pathways to the transport of surface derived organic matter

Table 5
Percentage contributions of sedimentary OM and modern surface derived OM (corrected for decay based on ^{14}C and ^{3}H ages of the groundwater). Scenario A, B and C represents two-component mixing of modern OM with sedimentary OM that is 1000, 3000 and 6000 years old respectively. Where values are not given the age of the sedimentary OM that is mixed is younger than the age of the sample and the model does not converge. ND denotes not determined as a result of insufficient OC in the sample.

Tubewell	C-14 enrichment	% Sedimentary OM			% Modern OM		
	(% modern)	A	B	C	A	B	C
TE11-12	99.07	8	3	2	92	97	98
TE11-20	87.94	–	40	23	–	60	77
TE11-55	60.50	–	–	65.7	–	–	34.3
ML01-9	93.83	54	20	12	46	80	88
ML01-29	71.65	–	93	54	–	7	46
ML01-37	72.57	–	90	53	–	10	48
TE51-12	91.08	78	29	17	22	71	83
TE51-20	85.47	–	47	27	–	54	73
TC31	89.99	87	31	18	13	69	82
TE61	89.61	91	33	19	9	68	81
ML02	75.06	–	82	48	–	18	52
TC45-12	71.03	–	95	56	–	5	44
TC45-20	93.75	55	21	12	45	80	88
ML03-7	91.45	75	28	17	25	72	83
ML03-24	87.88	–	40	24	–	60	77
ML03-42	83.52	–	54	32	–	46	68
ML04-8	ND	ND	ND	ND	ND	ND	ND
ML04-30	105.38	0	0	0	100	100	100
ML04-44	100.71	0	0	0	100	100	100
ML05	64.80	–	–	68	–	–	32

deep into the subsurface at this site. In this instance, stable and radiogenic isotopes demonstrate that groundwater received a significant contribution of rapidly transported pond derived recharge. We suggest that this observation may also be important regionally, and that the DOC pool of groundwater is likely to be dominated by surface derived DOC where ponds or clay windows act as point source(s) for transport of surface derived DOC through recharge.

In addition to the relationship we report here between groundwater residence time and groundwater As concentrations, we also observe a relationship between the age of organic carbon and As concentrations. These relationships can broadly be separated into three domains and classified according to the recharge environment that governs groundwater residence time and DOC. These domains are presented conceptually in Fig. 6. In the northern most domain of our field site within 1 km of the Mekong River, we observe a prevalence of relatively young (<750 years) DOC at depths of less than 15 m in tritium-active groundwater. This DOC likely represents a mixture of DOC transported during rapid recharge through clay windows with older DOC mobilized during slow recharge through surficial clays. The concentration of As in these groundwaters is exclusively greater than 35 μg/l. These higher concentrations are consistent with the proposal of Kocar et al. (2014) that rapid sedimentation and organic matter burial, driven for instance from flooding of the Mekong River during the monsoon season, results in more extensive As release and at greater depths within sediments. DOC ages generally increase with depth during the transition to tritium-dead groundwaters at depths greater than 15 m. Sedimentary organic matter therefore represents an increasingly large contribution of the total groundwater DOC pool in these deeper groundwaters.

In the central domain, rapid tritium-active recharge from ponds and clay windows gives rise to a groundwater DOC pool that is dominated by surface-derived DOC over the entire depth profile in the northern most extent of this domain at site ML04. The DOC in the remainder of the domain represents a mixture of sedimentary and surface derived DOC, despite the fact that the entire depth window is tritium-active. There does not appear to be any relationship with DOC age and depth, which suggests that a complex network of flow paths generates a non-linear age distribution of DOC in this domain. Groundwater As concentrations in this domain are exclusively lower than <35 μg/l. This may reflect the greater number of pore volumes of flushing these sediments have received, resulting in lower concentrations of As in higher permeability sediments compared to lower permeability sediments of similar age. Alternatively, the rapid nature of recharge may allow for the transport of oxidants that are able to consume organic carbon and sequester As from the groundwater. Either way, our results are in agreement with the predictions of Kocar et al. (2014) who suggest that locations where groundwater is dominated by recharge through high permeability pathways will be restricted to As concentrations of less than 60 μg/l.

The final domain represents recharge in the internal wetland basin. We sampled only 1 tubewell in this domain. Nonetheless, our data suggests slow recharge to depths of 60 m through relatively low permeability sediments. The DOC has an age of 3485 years at this depth, which is younger than organic matter in sediments at shallower

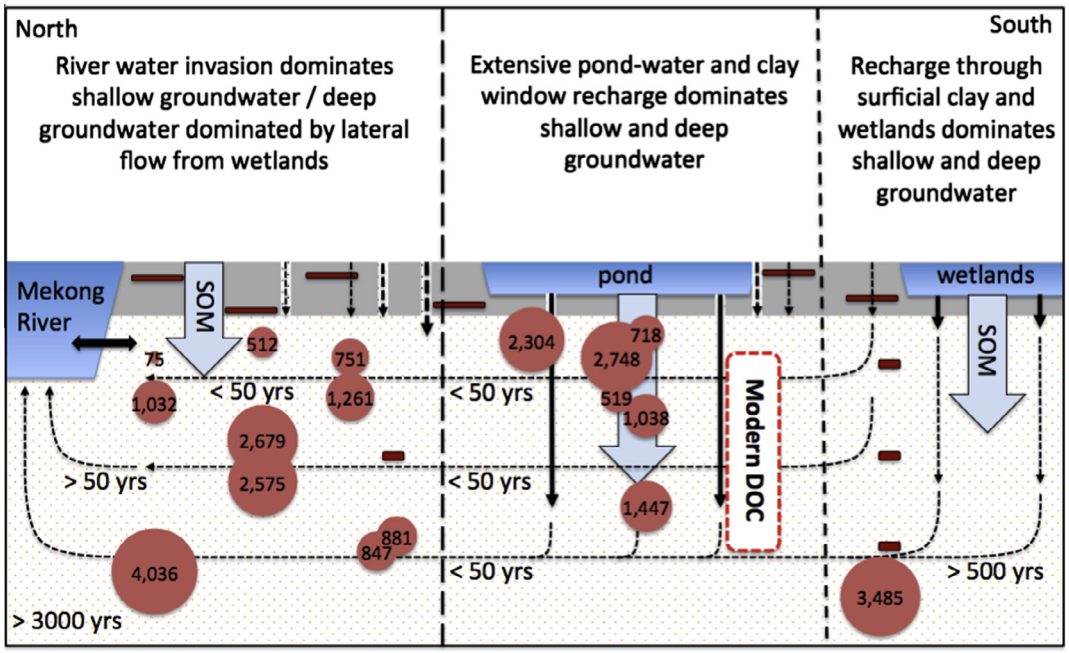

Fig. 6. Summary of the three-recharge domains that prevail at this site and the dominant form of organic matter associated with each domain. Circles represent organic matter ages, with larger circles representing older ages. The radiocarbon age of DOC given in the center of each circle. Approximate mean groundwater residence times are provided for the different domains based on integrated tritium and DI^{14}C data assuming flow from the wetland basin to the Mekong River following the study of Benner et al. (2008). Surface derived DOC is transported in recharge through the pond and clay windows in the southern most part of the central domain and dominates the DOC pool in tritium-active shallow and deep groundwater. DOC ages represent mixtures of surface and sedimentary organic matter elsewhere at this site.

depths (Lawson et al., 2013). This requires transport of younger OM to this depth. The concentration of As in this domain has previously been shown to exceed 500 μg/l (Polizzotto et al., 2008; Lawson et al., 2013). The high concentrations of As in this domain are consistent with the study of Stuckey et al. (2015a) who suggest that permanently saturated wetlands at this site experience only anaerobic metabolisms. As such, the consumption of DOC is dedicated to reductive processes that may ultimately result in the extensive release of As to groundwater.

Our results also provide interesting insights on the controls on As release in the aquifer systems of south Asia. We show here that shallow groundwater accrues As at a rate of approximately 1 μg/l/yr increase in DOC ^{14}C age compared to approximately 0.25 μg/l/yr increase in DOC age for deeper groundwaters (see Fig. 6). We recognize that this assessment does not link As concentrations to DOC age evolution along a flow path. Unfortunately, while the previous study of Benner et al. (2008) placed very useful constraints on the overall direction and timing of groundwater flow at the kilometer scale at the site, it still does not provide the appropriate resolution to account for small, local scale (10s–100s meter) fluid flow that is required to perform such a detailed, high resolution assessment. As such, we rely here on the broad classification of shallow and deep groundwater to account for the lack of resolution in our understanding of fluid flow. Ultimately, it is the local scale point source contributions of recharge from ponds and clay windows mixing with the larger scale, deeper fluid flow from the wetlands to the Mekong River that is likely to control the bulk geochemistry of groundwater at different locations at this site. Nonetheless, we believe this assessment provides useful first order constraints on the relationship between DOC age and associated As release. Indeed, this result is consistent with the findings in Vietnam of Postma et al. (2012) who show that As release is inversely proportional to the age of sedimentary organic carbon.

That As release is greater in shallow groundwater compared to deep groundwater at this site suggests that As is not only released in the near surface environment but also in the aquifer sediments, and over the entire length of the flow path. While we show a clear relationship between As concentration and DOC age in most locations, we also show that this relationship breaks down in areas where the DOC pool is dominated by modern DOC. This is because the fluids that transport modern DOC also deliver oxidants that result in the sequestration of As from groundwater to the sediment. This suggests that the rate and extent of arsenic release is therefore likely to be function of the amount of arsenic present in aquifer sediments, the distribution of competing electron acceptors introduced during recharge, and the age and hence residual reactivity of organic carbon that is available for anaerobic processes that release arsenic in these aquifers.

In addition to the mixing of multiple sources of DOC, the consumption of DOC in biogeochemical processes may also influence the radiocarbon age of organic carbon implicated in As release processes in these groundwater

systems. The removal of young DOC has been previously reported in the study of Raymond and Bauer (2001) who utilized measurements of $\delta^{13}C$ and changes in the ^{14}C age of DOC and particulate organic matter to demonstrate that bacteria preferentially utilise a ^{14}C enriched (young) source of DOC in estuarine and riverine environments. A more recent study by Mailloux et al. (2013) compared the radiocarbon age of microbial DNA isolated from groundwater with the radiocarbon age of DOC and OM. From this comparison they demonstrate that microbial communities within an aquifer system in Bangladesh where groundwater As concentrations exceed 200 μg/l utilize young OC. The preferential utilization of young DOC over older DOC would therefore result in older apparent radiocarbon ages of residual DOC. In this case, As may accumulate in groundwaters at greater rates than we estimate here because we have characterized only the age of residual DOC, and not that consumed in biogeochemical processes that may ultimately be responsible for driving As mobilization.

5. CONCLUSIONS

The data we present here demonstrate that recharge in close proximity to ponds has the potential to transport modern DOC to depths of 44 m and dominate DOC in groundwater, even in the absence of groundwater pumping. However, groundwater DOC more typically comprises a mixture of differently sourced OM, with contributions of young surface or near surface derived OM and older, sedimentary sourced OM clearly present. This suggests a potential dual role for both surface and sedimentary organic carbon in controlling the mobilization and distribution of As in these aquifer systems.

We show here a clear association between higher rates of As release in shallow groundwaters containing young DOC, and lower rates of As release associated with older sediments and DOC in deeper groundwater. We suggest that As release not only occurs during recharge through near surface sediments but also during transport through aquifer sands and likely partitions between sediment and groundwater over the entirety of its flow path in the subsurface. The relationship between the radiocarbon age of DOC and groundwater As may also suggest that younger sources of OM are preferentially consumed over older, residual sedimentary sources that have experienced a greater history of consumption in metabolic processes.

This study is the most extensive isotopic characterisation of the hydrological environment at an As hotspot under natural conditions to date. Taken in the appropriate context, this information provides a basis for comparison with aquifer systems where the extensive pumping of groundwater has disrupted subsurface flow and natural recharge conditions, potentially altering the distribution of the OM sources implicated in As release. Such information is of critical importance in developing process oriented models that are capable of accurately predicting how and where the current As hazard will change, and importantly at what rate. The results presented here suggest that the aquifer systems in largely undeveloped countries such as Cambodia are potentially at risk from anthropogenic interference that may influence the groundwater flow regime. In particular, activities such as groundwater pumping and the excavation of surficial clay deposits have the potential to significantly change the sources of groundwater recharge and the timescales over which recharge takes place. Such activities would likely also drive changes in the composition and distribution of groundwater DOC, which may ultimately influence the rate and extent of As release in these groundwaters.

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